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SEA WATER IMMERSION OF GEM II PROPELLANT

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ABSTRACT

Following the Delta II flight failure on 17 Jan 97, the question of continuing safety for solid propellant that had fallen into the Atlantic ocean arose. With this failure, approximately 200,000 pounds of HTPB solid propellant were released. While large amounts of propellant were consumed in burning fragments and ground impact explosions, considerable amounts of unburned propellant fell onto the land and into the Atlantic ocean. It was quickly found that propellant attacked by sea water became mushy, and ammonium perchlorate (AP) crystallized on propellant surfaces if it was allowed to dry. Concerns were raised that propellant washing ashore might present fire and/or explosive hazards. In response to these concerns, a program was initiated to investigate the effects of sea water on GEM II propellant as a function of time and its activity when burned, impacted, or subjected to friction. To date, results show that AP is leached out of the propellant at a straight line rate on a logarithmic plot. Friction and impact data on dried, sea water soaked propellant samples show no significant differences from virgin propellant. With wet sea water aged propellant samples, outer surface layers were found to be significantly less sensitive (friction and impact) than virgin propellant. The centers of these samples were found to be less sensitive than virgin propellant, but definitely more sensitive than their wet outer skin. In fuel fires, no difference was observed between virgin propellant and dried, sea water aged propellant burning. These samples ignited immediately with burning over all exposed surfaces. In contrast, wet sea water aged samples all had experienced ignition delays. Ignition delay usually paralleled propellant sample time of water exposure. In addition, these samples only burned from one face.

EXPERIMENTAL

SEA WATER AGING

GEM II propellant samples were aged in a portable swimming pool filled with Pacific ocean sea water. The dimensions of the swimming pool were 25 feet by 13.5 feet by 4.5 feet. It contained 10,500 gallons of sea water that had been previously sand filtered. The swimming pool, fitted with a circulation pump, was in a temperature controlled building. Temperature of the pool water varied from about 69 to 74°F. Propellant samples (1, 2 and 4 inch cubes) were placed in open plastic crate type boxes that had string or rope tied onto their ends for easy removal from the pool at periodic intervals for sample retrieval. Fifteen in. cubes were loosely held with plastic webbing. Some of the 1- and 2-in. propellant samples were buried in sand placed in open plastic crates. These crates were lined with sufficiently fine plastic mesh sheeting to keep sand from flowing out of the crates and exposing the samples.

Pacific sea water was used in this study because analysis showed no significant differences in mineral contents between it and Cape Canaveral sea water and because it was readily available from distance and cost standpoints. Simulated sea water was used to age 1-in. and 2-in. propellant cubes at the beginning of the program to check the validity of the program's experimental approach before all necessary materials and samples could be assembled to start the actual sea water aging.

FIRE TESTS

The 1-, 2- and 4-in. propellant cubes were burned in a 1-in. deep stainless steel tray that was filled with sand. They were remotely ignited using an electric match. Before a propellant sample was placed on the sand, the sand was saturated with isooctane fuel. Test videos enabled measurement of times-to-ignition and observation of burning vigor.

RESULTS

Based on the investigation of the Delta II accident at Cape Canaveral on 17 January 1997, it was determined that propellant samples, representative of the actual fragment sizes from the accident, would be aged in sea water. Then oxidizer depletion rates would be determined and safety testing (friction, impact and fire tests) would be performed. Propellant cubes (1-in., 2-in., 4-in. and 15-in.) were used in this aging study. The 15-in. cubes were representative of fragments involving the propellant's maximum web thickness. The 1-in., 2-in., and 4-in. cubes would demonstrate the validity of geometric scalability. Aging was conducted in Pacific sea water under ambient conditions.

Prior to the principle aging study, a preliminary aging study was initiated using samples obtained from a small propellant mix of Delta GEM propellant. Samples were both 1- and 2-in. cubes, aged in a 250 gallon container of simulated sea water. This preliminary study was performed to obtain aging data as soon as possible to validate the proposed program techniques and approaches before a larger 150 gallon propellant mix could be made at the Naval Air Weapons Center (NAWC) for use in the primary study.

Oxidizer or ammonium perchlorate (AP) depletion rates were determined for 1- and 2-in. propellant cubes aged in simulated sea (SS) water. Prior to aging, all surfaces of the cubes were freshly machined. Results are shown graphically in Figure 1. Both 1- and 2-in. cubes lost AP in an orderly manner with respect to size and time. The data showed that the proposed aging plan for the different sized propellant cubes was valid.

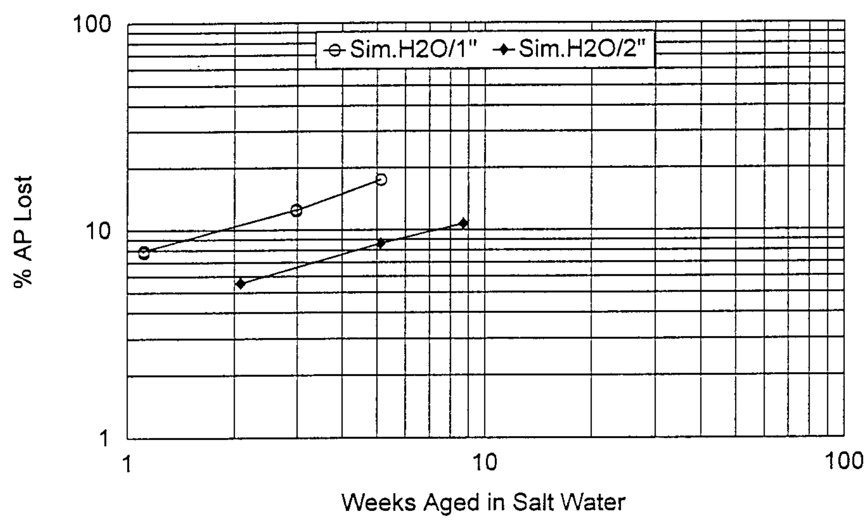

Figure 1. AP Depletion Rates for Propellant Aged in Sea Water

A 150 gallon mix of Delta GEM propellant was made at the Naval Air Weapons Center (NAWC) for this study. Propellant bars with square cross sectional areas exceeding 1-, 4- and 16-square inches were cast and cured as well as 15-in. cubes. Propellant bars were cut into 1, 2 and 4-in. cubes. All binder rich surfaces (resulting from casting operations) of sample cubes were removed. Removal of binder rich cube surfaces was intended to minimize differences between samples and accident produced fractured propellant in AP leaching rate during sea water aging. After cutting and surface prep operations, the cubes were weighed and measured prior to being immersed in a Pacific sea water filled pool inside plastic crates for the 1-, 2- and 4-in. cubes and loosely held plastic webbing for the 15-in. cubes. A portion of the 1- and 2-in. cubes were buried in sand contained in plastic crates prior to being immersed in the pool. These particular samples would simulate the effect of propellant buried under sand by tidal action of the ocean. Aging data is shown in Figure 2. Sea water aging data exhibits straight line relationships on a logarithmic plot. In addition, it shows the effect of differing weight to surface areas for the samples. It is interesting to note that the sand buried samples (1- and 2-in. cubes) appear to lose AP at the same rate as open water exposed samples. This was surprising because one would expect that the depletion rate would be

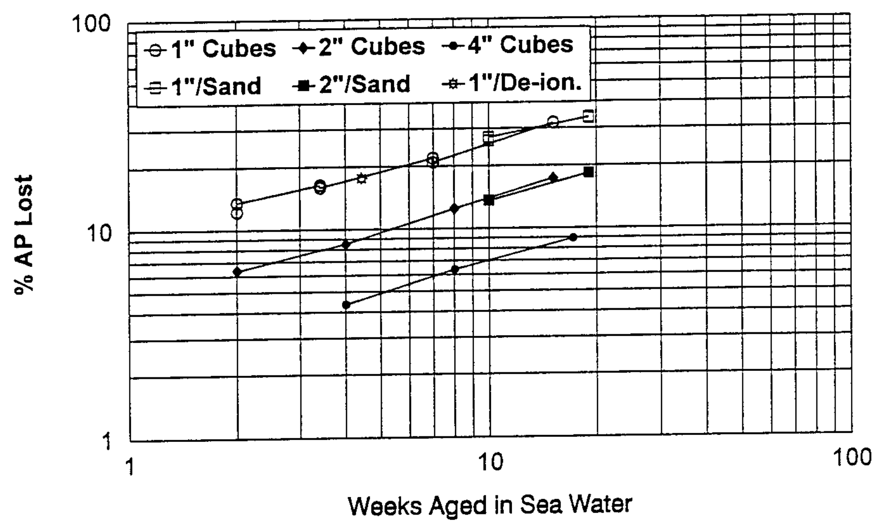

Figure 2. AP depletion for propellant aged in Pacific sea water.

for buried samples because of sand interference with diffusion. For reference purposes some 1-in. cubes were aged in deionized water. A measure of AP leaching was taken after one month. Since the measurement fell on the depletion line for sea water exposed and sand buried 1-in. cubes, fresh water and sea water leaching of AP appears to be the same. Further data collected for the deionized water process will show if the coincidence of AP leaching behavior with sea water continues.

This past fall blister-like raised areas began to appear on some of the 2- and 4-in. cubes. They did not appear on either the 1-in. or 15-in. cubes. There was no ready explanation for the phenomenon. An initial thought about blister bubble formation on propellant surfaces was that aluminum in the propellant had begun to react with sea water producing hydrogen gas. Hypodermic syringes were used to remove small gas samples from a few blister bubbles. Gas chromatographic analysis of the gas samples revealed nitrogen, oxygen and carbon dioxide. Thus evidence for hydrogen production was absent. Since air contamination was probable, only carbon dioxide could be positively identified as coming from the propellant samples. Cause for the carbon dioxide formation remains unexplained.

At some point during immersion in sea water propellant cubes began to have slippery, slimy surfaces. None of the cubes buried in sand became slimy. Microbiological life may be responsible for propellant cube sliminess and may, possibly, have been involved in the surface blister formation. During a heating system power outage, pool temperatures dropped about 15 degrees. Surface sliminess for 2- and 4-in. propellant cubes disappeared and there was an apparent reduction in blister population during this time period. That surface change reverted to a slimy condition once 75°F pool temperature was restored, seemed to be evidence for microbiological activity on the propellant samples.

Dimensions on wet sea water aged samples were measured. Resultant aging volumes for the different samples were calculated and divided by their initial or unaged sample volumes. In turn, these values were plotted against sea water exposure time to show how sample swelling increased with time. These results were expected to parallel oxidizer depletion rate data shown in Figure 2. A plot of the data can be seen in Figure 3. It should be pointed out that the volume relationships contain relatively large errors because sample irregularities are magnified with swelling. Regardless of inherent errors in the data, the general trends observed in Figure 2 were also observed with respect to sample volume.

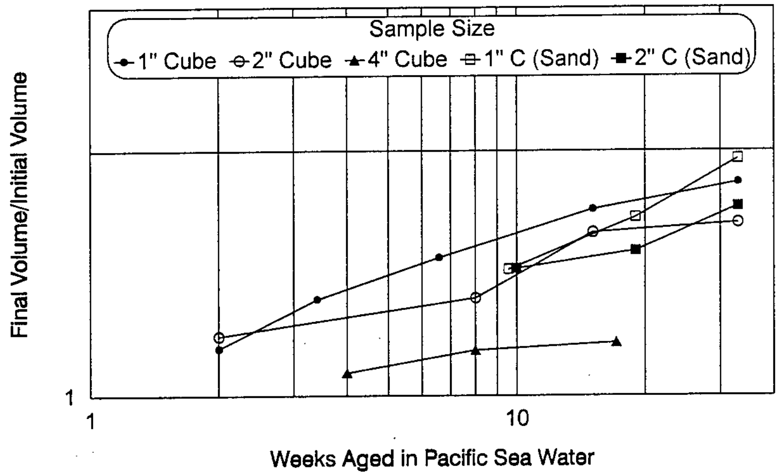

Figure 3. Relative Swelling Rates of Wet Aged GEM Propellant

During drying of oxidizer depleted samples, white spots appeared on sample surfaces. It was hypothesized that the spots were AP rather than sea salt. To check on this, Differential Scanning Calorimetry (DSC) thermograms were obtained on the spots of a representative dried sample and on some propellant grade AP. The results are shown in Figures 4 and 5. The essentially identical endothermic phase change curve shows that the spots were essentially AP.

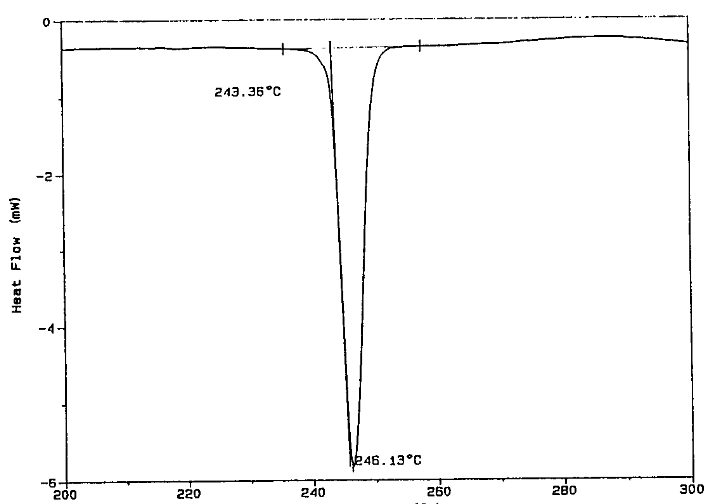

Figure 4. Differential Scanning Calorimeter Thermogram of White Crystalline Spots Located on the Surfaces of Dried Samples

Both impact and friction tests were run on some of the propellant cubes (dry and wet) that were submerged in the Pacific sea water. An Olin Mathieson, Model 7, Drop Weight Tester was used for the impact tests. Test samples had average dimensions of 0.30-in. diameter by 20/1000-in. thickness. A Julius Peters, Model 2, friction tester was also used. Average test sample dimensions were 1/2-in. x 1/4-in. x 20/1000-in. Most tests were run on both the outside skin or surface, where AP depletion was greatest, and on the central interior. A non-aged control was tested too. All samples were distinguished and identified by cut corners (number and position), notches (number and position) or by a combination of cut corners and notches (number and position).

Available data on 1- and 2-in. cubes is presented in Table 1. Impact data shows that wet aged cubes stand apart as being much less reactive and sensitive than their dried counterparts. The 102 kg-cm versus greater than 250 kg-cm impact values for samples 0-7 and 2c-1i in Table 1 show that this is especially true for outer skins or surfaces. Even the centers of the wet cubes were less sensitive than the centers of the dry cubes. It should be noted that the centers of 2-in. cubes were more sensitive than those

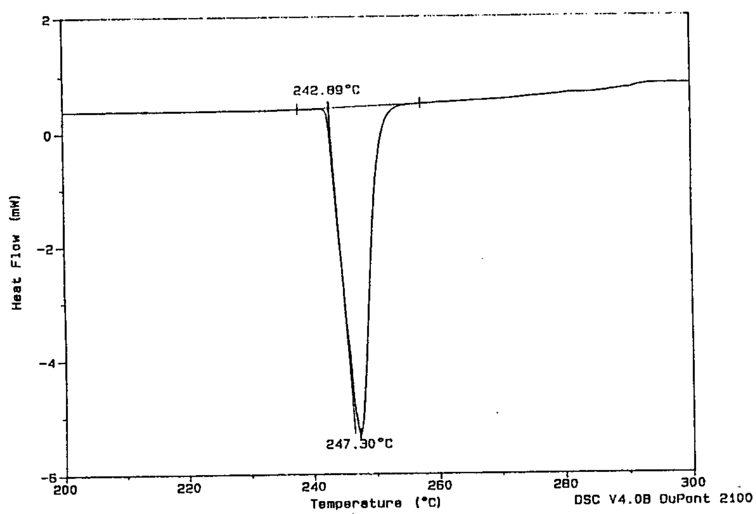

Figure 5. Differential Scanning Calorimeter (DSC) Thermogram of Ammonium Perchlorate (AP)

of 1-in. cubes, (e.g., 108 kg-cm for 2-in. cube sample 8 versus 132 kg-cm for 1-in. cube sample 2c-1i). Based on surface area and total sample thickness, this is not surprising. Friction data shows that the outer surface of the wet aged cubes are much less sensitive than their centers that remain similar in sensitivity to the dried samples. For example, >250 kg-cm and 132 kg-cm for sample 2c-1i skin and center, respectively. All wet, immersion aged cubes had wet interiors. This was determined by comparative observation of corresponding dried samples that had been extracted from wet cube centers.

Fire tests were also run on both wet and dry propellant cubes that had been submerged in sea water. A dry control sample was tested too. Test results are presented in Table 2. The sea water soaked, but dry, samples behaved very much like dry, untreated propellant. The dried cubes rapidly ignited. Once ignited, the flame front quickly spread over the entire surface of the cubes. Wet cubes were different. They required some added length of heating time before they could sustain combustion. Once combustion was sustained, only one face of the cube burned. In general, burning delay was directly related to sample size and to water exposure. Videos of these fire tests show an interesting phenomenon related to the wet water soaked samples. Before sustained wet propellant burning took place transitory burning of numerous small surface spots were observed.

Fire test 18 produced an interesting result. The external fuel fire burned for 300 seconds and extinguished, but the 2-in. cube sample had not ignited. After allowing the cube to cool, visual examination did not exhibit scorch or burn marks nor any cube face distortions. Although this cube was drier than it was at the start of the test, it still contained moisture.

Table 1. Friction and Impact Test Results of Aged GEM Propellant

Sample	Cube Size	Aging Time[a]	No Fires	Location/State	Impact, kg-cm	Frict.,E,kg-cm
Reference[b]		0.00	4 (7)	Dry	93	12.0
0-7	1"	2.00	5 (5)	Skin/Dry	102	9.6
2c-1i	1"	2.00	5 (5)	Skin/Wet	250[c]	28.8
"	1"	2.00	5 (5)	Center/Wet	132	14.4
3c-2io	1"	3.43	5 (5)	Skin/Dry	108	16.8
3c-3iio	1"	3.43	5 (5)	Skin/Wet	250[c]	36.0[d]
"	1"	3.43	3 (5)	Center/Wet	240	21.6
6c	1"	6.97	4 (5)	Skin/Dry	99	14.4
"	1"	6.97	3 (5)	Centre/Dry	96	-
4ccc	1"	6.97	5 (5)	Skin/Wet	250[c]	36.0[d]
"	1"	6.97	5 (5)	Center/Wet	141	21.6
2t	1"	9.97	3 (5)	Skin/Dry	96	14.4
"	1"	9.97	4 (5)	Center/Dry	99	-
3c-3ioo	1"	9.97	5 (5)	Skin/Wet	250[c]	36.0[d]
"	1"	9.97	5 (7)	Center/Wet	138	28.8
8	2"	2.00	5 (5)	Skin/Wet	250[c]	32.4
"	2"	2.00	4 (5)	Center/Wet	108	14.4
0-5cccd	2"	4.00	5 (5)	Skin/Wet	250[c]	36.0[d]
"	2"	4.00	4 (5)	Center/Wet	105	14.4
1	2"	8.00	5 (5)	Skin/Wet	250[c]	32.4
"	2"	8.00	4 (5)	Center/Wet	105	14.4
3cc-2ii	2"	9.97	5 (5)	Skin/Wet	250[c]	36.0[d]
"	2"	9.97	4 (5)	Center/Wet	114	14.4

a. Aging time in weeks

b. Propellant was not aged.

c. 250 kg-cm Impact value is upper limit for test.

d. 36.0 kg-cm friction value is upper limit for test.

In conducting burn tests for propellant cubes exposed to sea water, a relatively low level of isooctane flame was utilized. This mode of operation was intended to provide relatively long heating periods before propellant ignition occurred. This was an attempt to obtain more violent behavior in propellant burning than might be exhibited in a very strong totally engulfing fire. Low level of external flame in cube burning trials also allowed continuous visual observation of the propellant cube during burn testing. Since the quantity of isooctane fuel was not closely controlled and wind conditions varied during the burn testing, there was considerable variability in delay time to burn for wet propellant cubes. Samples 3c-1ii (Test 20) and 3cc (Test 9) had time-to-burn delays of 140 and 225 seconds, respectively. This was incongruous since sample 3c-1i had been water submerged for 3.4 weeks versus 2.0 weeks for sample 3cc. Normally, delay times to burning would have been longer for the propellant exposed to sea water longer.

The propensity of wet propellant samples to burn on one side might be linked to the fire resistance of AP poor surfaces with good insulating properties that reduce heat flux to the interior propellant provided by the isooctane donor and propellant burning flames. Propellant sample wetness throughout and external flame asymmetry probably influenced the tendency for asymmetric burning.

CONCLUSIONS

It was concluded tht AP leached out of GEM propellant exposed to sea water in a straight line manner on a logarithmic plot. Friction and impact data on dried aged propellant samples showed no significant increased burning hazard compared with propellant not exposed to water. The outer surface layers of wet propellant samples were significantly less sensitive (to friction and impact) than virgin propellant. The centers of the wet samples were found to be less sensitive than propellant not exposed to water, but definitely more sensitive than wet propellant sample

Table 2. Effect of Aging Time and Sample Size on Fire Test Results

Test	Sample	Aging Water	Cube/State	Soak Time[a]	Time to Burn[b]
1	Control	None	1"/Dry	0.00	0
2	5-5i	S[c]	1"/Wet	1.11	60
3	7	S	1"/Dry	1.11	0
7	2-1i	S	1"/Dry	2.97	0
8	1-1o	S	1"/Wet	2.97	125
15	1-1i	S	1"/Dry	5.12	0
16	3-1i	S	1"/Wet	5.12	225
11	6t	S	2"/Dry	2.08	0
12	3	S	2"/Wet	2.08	90
17	2c	S	2"/Dry	5.12	0
18	1	S	2"/Wet	5.12	>300[f]
25	2t	S	2"/Wet	5.12	200
26	5	S	2"/Dry	8.69	0
27	0	S	2"/Wet	8.69	270
4	3	C[d]	1"/Wet	1.11	55
5	0	C	1"/Dry	2.97	0
6	5	C	1"/Wet	2.97	115
9	3cc	P[e]	1"/Wet	2.00	225
10	3cd	P	1"/Dry	2.00	0
19	2c-2io	P	1"/Dry	3.43	0
20	3c-1ii	P	1"/Wet	3.43	140
28	4cd	P	1"/Dry	6.97	0
29	5 3(90)	P	1"/WEt	6.97	425
32	2t-3iid	P	1"/Dry	9.97	0
33	0	P	1"/Wet	9.97	348[g]
13	6t	P	2"/Dry	2.00	0
14	6c	P	2"/Wet	2.00	60
21	3cc-1i	P	2"/Dry	4.00	0
22	2c-2io	P	2"/Wet	4.00	120
30	2c	P	2"/Dry	8.00	0
31	0-2c	P	2"/Wet	8.00	352
34	3cc-200	P	2"/Dry	9.97	0
35	4ccc-1op	P	2"/Wet	9.97	354
23	3tt	P	4"/Dry	4.00	0
24	6t	P	4"/Wet	4.00	120

a. Time in weeks
b. Approximate time in seconds
c. Simulated seawater
d. Cape Canaveral water
e. Pacific seawater
f. Sample did not burn before fuel flame expired.
g. Fire intensity was greater than that of Test 29.

surfaces. In fuel fires, no difference could be observed between burning fresh propellant and dried, but aged propellant. All samples ignited immediately and burning spread over all exposed surfaces. Finally, it was concluded that all wet aged samples experienced ignition delays. Ignition delays were directly related to water immersion time. In addition, these samples only burned on one face leaving an oxidizer poor rubber shell.